Vapor–Liquid Equilibrium Thermodynamics of \( N_2 + CH_4 \):
Model and Titan Applications

W. Reid Thompson

Laboratory for Planetary Studies, Space Sciences Building, Cornell University, Ithaca, New York 14853

AND

John A. Zollweg and David H. Gabis

Laboratory for Chemical Thermodynamics, School of Chemical Engineering, Cornell University, Ithaca, New York 14853

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INTRODUCTION

Titan’s Atmosphere

Prior to the Voyager encounters with Saturn and its satellites, the presence of CH\(_4\) had been known for decades (Kuiper 1944). While its abundance was uncertain, the strengths of the observed bands implied an equivalent base pressure of at least 15 mbar (Trafton 1972). Pressure broadening of the 1.1-\(\mu\)m band indicated the presence of other undetected gases (Lutz et al. 1976), and models of the possible photolysis of NH\(_3\) early in Titan’s history (Atreya et al. 1978, Chang et al. 1979) suggested that N\(_2\) was a likely candidate. Voyager measurements proved N\(_2\) to be an important constituent along with CH\(_4\): prominent ionospheric emission by N\(_2\) detected by the Voyager UVS experiment (Broadfoot et al. 1981) along with a molecular mass \(=28\) Da implied by the combined constraints of the radio occultation (RO) experiment and IRIS measurements (Tyler et al. 1981, Hanel et al. 1981) showed the atmosphere to be N\(_2\)-dominated with a few percent of CH\(_4\). At an altitude \(z \approx 1400\) km, the gas-phase CH\(_4\) mole fraction \(Y_{CH_4} \approx 8\%\) (Smith et al. 1982), while the combined constraints of the IRIS-observed CH\(_4\) band and RO limit stratospheric \(Y_{CH_4}\) to 1.0–1.7\% for an atmosphere composed only of N\(_2\) and CH\(_4\) (Lellouch et al. 1989). For some solutions of Titan’s range of allowed atmospheric thermal structures (Lellouch et al. 1989), a mean molecular mass consistent with the presence of an additional heavier component is implied: if present, this constituent is expected...
to be Ar. The range of $Y_{CH_4}$ is 0.5–3.4% if Ar is present. (There is no direct evidence for Ar; the UVS upper limit at high altitudes suggests only a mole fraction <40% in the troposphere (ibid.).)

The extreme temperature ranges allowed are 70.5 K < $T < 74.5$ K for the tropopause (at pressure $p = 0.1$ bar) and 93.1 K < $T < 100.6$ K for the surface (at pressure $p = 1.5$ bar) (Lellouch et al. 1989). Titan’s surface temperature decreases by only ~2 K from the equator to the poles (Flasar et al. 1981). Thus, knowledge of the properties of Titan’s atmospheric gases and condensates over a temperature range of 70 to ~100 K is required.

The atmosphere at the surface is in equilibrium with oceans or lakes of C$_2$H$_6 +$ CH$_4 +$ N$_2$ solution (Lunine et al. 1983, Thompson 1985) which contain other dissolved solutes, both organic and inorganic (Raulin 1987, Dubouloz et al. 1989). The composition of the surface liquid and the surface value of $Y_{CH_4}$ are strictly coupled (Thompson 1985) but neither is well constrained at present. If $Y_{CH_4} \approx 2\%$ in Titan’s troposphere, condensation of clouds will occur through some altitude range. The presence of CH$_4$ in condensed form is necessary to produce a satisfactory match to Titan’s IRIS-measured thermal emission spectrum from 200 to 600 cm$^{-1}$ (Courtin 1982, Thompson and Sagan 1984, Toon et al. 1988, McKay et al. 1989). While both large column densities of radius $r = 0.1 \mu m$ droplets and much lower column densities of $r \approx 100 \mu m$ droplets can improve the match to the Voyager IRIS spectra (Toon et al. 1988), radiative balance and microphysical arguments suggest that diffuse clouds with large droplets are more likely (Toon et al. 1988, McKay et al. 1989). These clouds are actually not pure CH$_4$, but a solution of N$_2$ in CH$_4$ (Thompson 1985, Thompson et al. 1990), which will be liquid for $T > 80.6$ K ($z \approx 14$ km) in the troposphere but, depending on the degree of supercooling, will be a solid solution at higher altitudes.

Equilibrium Thermodynamics of N$_2 +$ CH$_4$

To be able to constrain the saturation profile of Titan’s atmosphere and compute the equilibrium between the gas and the cloud condensate, it is necessary to derive a reliable thermodynamic model for binary equilibrium in the N$_2 +$ CH$_4$ system. The N$_2 +$ CH$_4$ system is substantially nonideal (Thompson et al. 1990). A simple model for the C$_2$H$_6 +$ CH$_4 +$ N$_2$ ternary was obtained by Thompson (1985), but it is not very good for calculations of the N$_2 +$ CH$_4$ binary because of the inaccuracies introduced by the very limited ternary data set. The binary was modeled using a regular solution formulation by Dubouloz et al. (1989), but shows systematic deviations from experimental measurements of ~10%. An empirical representation fit to mutually consistent data between the CH$_4$ triple point of 90.68 K and 105.0 K was derived by Thompson et al. (1990). This model is quite accurate and simple to use, but does not make full use of the constraints imposed by thermodynamic consistency. Kouvaris and Flasar (1991) have used an integration of the Gibbs–Duhem equation to compute the vapor composition along isopleths (lines of constant composition). This method is thermodynamically rigorous but requires accurate experimental data at the temperatures where it is to be applied, and is rather difficult to utilize for general calculations.

Many of the limitations and possible experimental biases of previous models can be overcome by formulating a model in which the temperature dependence is built-in, and in which both the experimental data at a given $T$ and the $T$-dependence of the model are strongly constrained by thermodynamic theory. The confidence of $T$-dependence in a model can be greatly improved by simultaneously utilizing vapor–liquid equilibrium (VLE) and heat of mixing (excess enthalpy, $H^E$) measurements. Obtaining a reliable $T$-dependence in the model is especially important since data that can be rigorously evaluated for consistency only exist above 90.68 K, while most or all of Titan’s cloud condensates at lower temperatures.

In this paper, using an accurate nonideal equation of state for N$_2 +$ CH$_4$ gas, selected VLE data demonstrated to be thermodynamically consistent, and a maximum likelihood fitting technique which uses both VLE data and $H^E$ measurements, we derive a robust model for the N$_2 +$ CH$_4$ system which can be readily utilized in accurate calculations for low-$T$ (≤ 125 K) outer planet applications.

THERMODYNAMICS AND MODEL

The free energy of mixing of $n$ moles of an ideal liquid is $n \Delta G^i = nRT \sum X_i \ln X_i$, where $R$ is the universal gas constant and $X_i$ is the liquid-phase mole fraction of species $i$. For real solutions, thermodynamic excess quantities are used to express the deviations from ideality: $\Delta G_{tot}^i = \Delta G^i + G^E$. The excess free energy of mixing for the liquid is defined as

$$nG^E = nRT \sum X_i \ln \gamma_i = n \sum X_i \mu_i^E,$$

where $\gamma_i$ is the activity coefficient and $\mu_i^E$ is the excess chemical potential of component $i$.

The partitioning of molecules between the liquid and gas phase is determined by nonideal interactions in both phases. For ideal gaseous and liquid states the equilibrium would be expressed by $p_i = Y_i p = X_i p_i^{sat}$ (Raoult’s law) where $p_i$ is the partial pressure of species $i$, $Y_i$ is the mole fraction of $i$ in the gas, and $p_i^{sat}$ is the vapor pressure of pure $i$. The more general expression is
\[ \phi_i Y_i p = \gamma_i X_i p_i^{\text{sat}}, \]  
\[ \gamma_i = \gamma_i \Theta(0, p) \]  
\[ p_i^{\text{sat}} = p_i^{\text{sat}} \phi_i \Theta(p_i^{\text{sat}}, 0), \]  
where \( \gamma_i \) is the fugacity coefficient of the gas at pressure \( p \), \( \phi_i \) is \( \phi_i \) at pressure \( p_i^{\text{sat}} \), and the terms \( \Theta(0, p) \) and \( \Theta(p_i^{\text{sat}}, 0) \), respectively, correct \( \gamma_i \) and \( \phi_i \) to standard reference states (see Prausnitz et al. 1967). (The overall Poynting correction \( \Theta(p_i^{\text{sat}}, p) \rightarrow \Theta(0, p)\Theta(p_i^{\text{sat}}, 0) \).)

Modeling the thermodynamics of VLE usually consists of adopting a form for \( G^E \) (motivated by some combination of theory and practical utility) and using a form of the Gibbs-Duhem relation

\[ RT \ln \gamma_i = \mu_i^E = \frac{\partial}{\partial n_i} [n_i G^E]_{T, p, n_j} \]  

to derive activity coefficients. When the \( \gamma_i \) are in hand, iterative techniques (see Prausnitz et al. 1967) can be used to find the mole fractions \( X_i \) and \( Y_i \) consistent with a given \( T \) and \( p \). For a system in phase equilibrium, the Gibbs phase rule states that for \( n_c \) components (i) and \( n_p \) phases, the number of degrees of freedom \( \theta \) is

\[ \theta = n_c - n_p + 2. \]

A two-component system with a gas phase and one liquid phase is then completely defined by \( p \) and \( T \), whereas \( n_c - 2 \) additional quantities (some of the \( X_i, Y_i \), or related values) must be known to fully determine the state of two-phase multicomponent systems.

**Equations of State and Vapor Pressure**

While other equations of state can be employed for the nonideal gas (see Kidnay et al. 1985), we use the familiar virial equation of state which, including terms up to second order, can be written as

\[ Z = \frac{pv}{RT} = 1 + B_{\text{mix}} v^{-1} + C_{\text{mix}} v^{-2}, \]

where \( Z \) is the compressibility factor, \( v \) is the molar volume, and the gas mixture virial coefficients are

\[ B_{\text{mix}} = Y_1^2 B_{11} + 2Y_1 Y_2 B_{12} + Y_2^2 B_{22}, \]
\[ C_{\text{mix}} = Y_1^2 C_{111} + 3Y_1^3 Y_2 C_{112} + 3Y_1 Y_2^2 C_{122} + Y_2^3 C_{222}. \]

We have found that the computational strategy of Hayden and O’Connell (1975) yields second virial coefficients \( B_{ij} \) that correspond closely to experimental measurements. Because of this good agreement and the limitations of experimental data (especially for cross-coefficients at relevant temperatures), we use that method to calculate all \( B_{ij} \)'s. We compute the third virial coefficients for pure components \( C_{ii} \) using the method of Orbey and Vera (1983), and employ an extension of the Prausnitz (1969) combining rules to compute the cross-coefficients. See the Appendix for a detailed description of the calculation of virial coefficients.

The vapor pressures of the pure components are computed using the equations and constants derived by Iglesias-Silva et al. (1987). Their method accurately spans the range between triple point and critical point temperatures. At the temperatures relevant here, the computed vapor pressures for \( N_2 \) agree closely with those computed by the third-order virial expressions of Brown and Ziegler (1980), so the two methods for computing \( \rho_i^{\text{sat}} \) are nearly equivalent. The same is true for \( CH_4 \) down to its triple point, \( T_{\text{tr}} = 90.68 \text{K} \), but in Titan’s atmosphere condensation to the liquid state occurs down to \( 80.6 \text{K} \). Computing saturation conditions below the \( CH_4 \) triple point requires a vapor pressure equation accurate for the supercooled liquid. While the parameterization of Brown and Ziegler has no constraining principle for extrapolation through the triple point, the Iglesias-Silva equation is constrained to match a theoretical asymptotic form at \( T_{\text{tr}} \), and therefore should more accurately predict the vapor pressure of the supercooled liquid.

Details of the calculation of vapor pressures are given in the Appendix.

**Functional Form for \( G^E \)**

We use a three-term Redlich-Kister expansion (Redlich et al. 1952) to obtain a functional form for \( G^E \) in terms of the liquid mole fractions \( X_i \):

\[ G^E = RT X_1 X_2 [a + b(X_1 - X_2) + c(X_1 - X_2)^2], \]  
\[ (7a) \]

where we denote \( N_2 \) by subscript 1 and \( CH_4 \) by subscript 2.\(^3\)

In order to describe the thermodynamics of the system accurately over a wide range of temperatures we allow the three constants \( a, b, \) and \( c \) to be functions of inverse \( T \):

\[ a = a_0 + a_1 T^{-1} + a_2 T^{-2}, \]
\[ b = b_0 + b_1 T^{-1}, \]
\[ c = c_0 + c_1 T^{-1}. \]  
\[ (7b) \]

The corresponding form for \( H^E \) is obtained using the Gibbs-Helmholtz relation

\(^3\) The form of Eq. 7a derives from the boundary condition \( G^E = 0 \) at \( X_i = 0 \) (\( i = 1, 2 \)). The simplest equation obeying this condition is \( G^E = aRTX_1X_2 \), a “one-term” equation. To fully account for nonideal effects in the \( N_2 + CH_4 \) system, we find that a three-term expansion with temperature-dependent coefficients is required.
\[
H^E = \left[ \frac{\partial (G^E/T)}{\partial (1/T)} \right]_{p, x}
\]
\[
= RT X_1 X_2 [a' + b'(X_1 - X_2) + c'(X_1 - X_2)^2], \quad (8)
\]
where \(a' = a_1 T^{-1} + 2a_2 T^{-2}, \ b' = b_1 T^{-1}, \) and \(c' = c_1 T^{-1}. \) The forms for the activity coefficients obtained from Eqs. (7) and (3) are

\[
\ln \gamma_1 = X_2^2 [a - (1 - 4X_1) b + (1 - 8X_1 + 12X_1^2) c] = X_2^2 [(a + 3b + 5c) - 4(b + 4c)X_2 + 12cX_2^2], \quad (9)
\]
\[
\ln \gamma_2 = X_1^2 [a + (1 - 4X_2) b + (1 - 8X_2 + 12X_2^2) c] = X_1^2 [(a - 3b + 5c) + 4(b - 4c)X_1 + 12cX_1^2].
\]

Once the constants are determined, these \(\gamma_i\) can be used to achieve iterative solutions of the vapor-liquid equilibrium (Eq. 2).

**Maximum Likelihood Fitting Method**

A method commonly used to fit VLE data in a thermodynamically consistent way is that of Barker (1953), where the analytical expression for \(G^F\) is related to total pressure via Eqs. (3) and (9), or some analogous expression, and \((p, T, X)\) data are fit in a least-squares sense to obtain the parameters in the \(G^F\) representation. For our representation of \(G^F\), if we take \(\gamma'_i = \gamma_i\) and \(p_i^{\text{set}} = p_i^{\text{fit}}, \) the Barker method is equivalent to a least-squares fit to the equation

\[
p_{\text{set}} = \left( X_i / \phi_i \right) p_i^{\text{fit}} \exp[X_2^2 (a + 3b + 5c) - 4(b + 4c)X_2 + 12cX_2^2] + \left( X_i / \phi_i \right) p_i^{\text{fit}} \exp[X_1^2 (a - 3b + 5c) + 4(b - 4c)X_1 + 12cX_1^2].
\]

Here we replace the simple least-squares approach of the standard Barker method with a maximum likelihood estimation of the parameters which allows for uncertainties in all measured quantities. This approach varies the parameters and measured quantities to maximize the probability that the set of observations will be obtained given the model and the measurement uncertainties (Skjold-Jørgensen 1983). As with simpler least-squares methods, systematic errors within the data will bias the parameter estimates, so we examine the deviations of pressures and compositions from the model and retain only data which are thermodynamically consistent.

An additional advantage of this model is its ability to accommodate \(H^E\) data simultaneously with VLE measurements. \(H^E\) data strongly constrain the temperature dependence of \(G^F\) through (8) and facilitate the detection of, and/or limit the bias of, VLE data which are inconsistent with a smooth temperature dependence of \(G^F\) (see Kidnay et al. 1985). (For a detailed description of the model contact J. A. Zollweg).

**EXPERIMENTAL DATA**

An extensive review and evaluation of the thermodynamics of \(N_2 + CH_4\) in the gas and liquid phases was performed by Kidnay et al. (1985). In this study thermodynamic consistency tests were used to evaluate VLE data: departures of the computed quantity \((G^E/T)_{X = 0.5}\) from the curve predicted by excess enthalpy \((H^E)\) measurements (see Eq. 8) identify inconsistent data. We have both screened the data with an initial test and examined the point-by-point deviations of candidate experimental measurements from our model predictions: since our model is by nature thermodynamically consistent, this serves as a similar but more detailed test than that used by Kidnay et al. We find that the data of McClure et al. (1976) at 90.68 K, of Parrish and Hiza (1974) at 95.0, 100.0, 105.0, and 110.0 K, of Kidnay et al. (1975) at 112.0 K, and of Stryjek et al. (1974) at 113.71 K provide the most consistent collection for a low temperature model. With the exception of the addition of Kidnay et al. (1975), these sources form a subset of those judged consistent by Kidnay et al. (1985). In our model, \(H^E\) data are fit simultaneously with the VLE data: we use the \(H^E\) measurements of McClure et al. (1976) at 91.5 and 105.0 K along with the selected VLE data in the maximum likelihood calculations.

**THE \(N_2 + CH_4\) THERMODYNAMIC MODEL**

**Parameter Values and Model–Experiment Comparisons**

The maximum likelihood values of the parameters and their approximate uncertainties assuming no correlations (the square roots of the diagonal elements of the covariance matrix) are shown in Table I. The model predictions and residuals are compared with selected experimental data relevant to Titan conditions in Fig. 1. The deviations of the data used in the analysis are small and/or random, indicating good consistency. We list the root-mean-square deviations for all the data sets utilized in Table II.
TABLE I
Thermodynamic Model Parameters for the N₂–CH₄ System

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Covariance ¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>a₀</td>
<td>0.8096</td>
<td>0.0181</td>
</tr>
<tr>
<td>a₁</td>
<td>-52.07</td>
<td>3.56</td>
</tr>
<tr>
<td>a₂</td>
<td>5443</td>
<td>175</td>
</tr>
<tr>
<td>b₀</td>
<td>-0.0829</td>
<td>0.0111</td>
</tr>
<tr>
<td>b₁</td>
<td>9.34</td>
<td>1.04</td>
</tr>
<tr>
<td>c₀</td>
<td>0.0720</td>
<td>0.0268</td>
</tr>
<tr>
<td>c₁</td>
<td>-6.27</td>
<td>2.57</td>
</tr>
</tbody>
</table>

TABLE II
Deviations for Individual Data Sets

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ΔPₓrms (bar)</th>
<th>ΔXₓrms</th>
<th>ΔYₓrms</th>
</tr>
</thead>
<tbody>
<tr>
<td>90.68</td>
<td>0.0042</td>
<td>0.0025</td>
<td></td>
</tr>
<tr>
<td>95.00</td>
<td>0.0041</td>
<td>0.0233</td>
<td>0.0134</td>
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<tr>
<td>100.00</td>
<td>0.0033</td>
<td>0.0174</td>
<td>0.0112</td>
</tr>
<tr>
<td>105.00</td>
<td>0.0200</td>
<td>0.0296</td>
<td>0.0046</td>
</tr>
<tr>
<td>110.00</td>
<td>0.0200</td>
<td>0.0251</td>
<td>0.0071</td>
</tr>
<tr>
<td>112.00</td>
<td>0.0202</td>
<td>0.0543</td>
<td>0.0265</td>
</tr>
<tr>
<td>113.71</td>
<td>0.0642</td>
<td>0.0114</td>
<td>0.0225</td>
</tr>
</tbody>
</table>

FIG. 1. Comparison of experimental data and model predictions. (a) Total pressure versus composition, pressure deviations, and composition deviations. Open symbols represent vapor compositions Yᵢ and filled symbols represent liquid compositions Xᵢ at total pressure (p). (b) Excess enthalpy versus composition, and enthalpy deviations. See text for references appropriate to each temperature.
There are no VLE measurements along isotherms (and therefore amenable to the present analysis) below the CH$_4$ triple point $T_{tp} = 90.68$ K. Such data are difficult to obtain. Yet much of the altitude range at which condensation may occur in Titan’s atmosphere lies below this temperature; for the nominal model of Lellouch et al. (1989) the surface temperature is 93.9 K, and 90.68 K is reached just below $z = 3$ km. Condensation to the liquid state occurs up to $z = 14$ km, $T = 80.6$ K. Above this altitude the liquid is metastable with respect to a solid solution (Thompson 1985, Thompson et al. 1990).

There are data which span $(p, T)$ regimes relevant to Titan, although their form prevents direct assessment of thermodynamic consistency and inclusion in our model. Omar et al. (1962) and Fuks and Bellemans (1967) plot total pressure $p_{tot}$ versus $T$ along lines of constant composition (isopleths). The data of Omar et al. are more extensive, with $p_{tot}$ ranging from about 1 bar down to the vapor–liquid line. Kouvaris and Flasar (1991) have computed vapor compositions along isopleths by integration of the Gibbs–Duhem equation, using selected data from Omar et al. along with isopleths estimated from interpolated isothermal data to define the paths.

The strong constraints on temperature dependence imposed by the functional form and the inclusion of $H^e$ data in our model should allow it to be used with reasonable confidence at these lower temperatures. In particular, we can compute the model-predicted isopleths at the compositions studied by Omar et al. (1962) and assess the differences. The results are shown in Fig. 2. Some of the isopleths agree well with the model, while others show large deviations. The $X_{N_2} = 0.037$ isopleth deviates greatly from the model; Kouvaris and Flasar also found these data to be suspect, and did not include them in their analysis. Both the position and the implied slope of the sequence of points for $X_{N_2} = 0.128$ also deviate substantially. For the other isopleths the experimental points match the model lines better. Because several of the isopleths agree very well with the computed lines and the offsets do not seem to be systematic, we feel this comparison validates the model for Titan applications both above and below 90.68 K—in fact, the model seems reliable down to the $N_2$–CH$_4$ eutectic at 62.5 K. The systematic offsets of some isopleths of Omar et al. from the model calculations suggest that those isopleths actually correspond to different liquid phase compositions than Omar et al. reported. We believe this results from a substantial uncertainty in measurements of the liquid phase composition in their work.

APPLICATIONS OF THE MODEL

Gas Saturation and Cloud Composition in Titan’s Atmosphere

We now use the model to compute the equilibrium between the gas and condensates in Titan’s atmosphere. The $p$–$T$ profile for Titan’s atmosphere has been reported by Lindal et al. (1983) and reanalyzed with allowances for atmospheric Ar and CH$_4$ content by Lellouch et al. (1989). The nominal profile computed by Lellouch et al. for the Ar-free case is very similar to that of Lindal et al., on which we base the saturation and composition profiles here. Our model describes the $N_2$–CH$_4$ binary and does not include Ar. Lellouch et al. included Ar in their equilibrium condensation model, but their regular solution model is relatively inaccurate for all species (Kouvaris and Flasar 1991).
Since there is no direct evidence for Ar and its presence would not produce major changes in the results, we leave its inclusion for further work.

Pure component and gas mixture properties along the nominal $p-T$ profile are shown in Table III. We compute the vertical profiles of CH$_4$ saturation mole fraction $Y_{CH_4}$ and of condensate composition $X_{N_2}$ by iteration from the surface up to the tropopause. The surface value of $Y_{CH_4}$ is probably controlled by the composition of primarily C$_2$H$_6$-CH$_4$-N$_2$ liquid at Titan's surface (Lunine et al. 1983, Thompson 1985, Dubouloz et al. 1989). A minimum of 700 m of C$_2$H$_6$ would be produced...
over geologic time at current photochemical rates (Yung et al. 1984), but since we do not know the equivalent depth or composition of the oceans, $Y_{CH_4}$ is limited only by the constraint that the $T$ profile of the troposphere is less steep than a wet adiabat or pseudoadiabat, which would seem to limit condensation to altitudes above $\sim 5 \text{ km}$.

The $Y_{CH_4}$ and $X_{N_2}$ profiles are shown in Table IV and Fig. 3; we also show the value $Y_{CH_4}^0$ that would apply if $N_2$ were not accounted for. Throughout the troposphere the gaseous mole fraction of CH$_4$ required for condensation is $10$–$20\%$ less than that required to condense pure CH$_4$. The $N_2$ mole fraction in the liquid $X_{N_2} = 0.16$ at the surface and increases to 0.28 at $z = 14 \text{ km}$. Above this altitude (below 80.6 K) freezing should occur, so the further increase of $X_{N_2}$ to its maximum of 0.29 at $z = 20 \text{ km}$ applies only to the metastable liquid—the solubility of $N_2$ in the solid is typically 8–10\% less in this region (Omar et al. 1962, see Thompson 1985). (Ar may further reduce the freezing point, but probably not by large amounts. See Van’t Zelfde et al. (1968) for the Ar–CH$_4$ solid–liquid phase diagram.) In a rising gas parcel, condensation continues to occur up to $z = 28 \text{ km} (T = 73.5 \text{ K})$; above this level, gaseous CH$_4$ retains its minimum value $Y_{CH_4} = 0.020$ into the stratosphere.

In Fig. 4 we compare the results of our model with the empirical representation of Thompson et al. (1990), with the results plotted by Kouvaris and Flasar (1991) resulting from their integration along isopleths, and with the simpler estimates which result from assuming an ideal solution (Raoul’t law) or (for $N_2$ solubility) a gas dissolving sparingly in a solvent (Henry’s law). In Fig. 4a we examine the predictions of $Y_{CH_4}$. The saturation values predicted by Thompson et al. (1990) are virtually identical to those computed from our detailed model, and the results of Kouvaris and Flasar (1991) for $Y_{CH_4}$ are also similar. The calculations of Kouvaris and Flasar are subject to the accuracy of $p_\text{sat}$ and liquid compositions in individual data sets, while direct parametric modeling of the VLE data without implicit constraints as in Thompson et al. (1990)

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### TABLE IV

**Composition and Heat of Condensation for Nominal Atmospheric Profile**

<table>
<thead>
<tr>
<th>$z$ (km)</th>
<th>$T$ (K)</th>
<th>$P$ (bar)</th>
<th>$Y_{CH_4}$</th>
<th>$Y_{N_2}$</th>
<th>$Y_{O_2}$</th>
<th>$Y_{Ar}$</th>
<th>$H^\circ$ (J/mol)</th>
<th>$\Delta H^\circ$ (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>94.0</td>
<td>1.500</td>
<td>0.118</td>
<td>0.164</td>
<td>0.109</td>
<td>0.161</td>
<td>1.839</td>
<td>1.022</td>
</tr>
<tr>
<td>0.5</td>
<td>93.3</td>
<td>1.490</td>
<td>0.112</td>
<td>0.150</td>
<td>0.103</td>
<td>0.167</td>
<td>1.830</td>
<td>1.024</td>
</tr>
<tr>
<td>1.0</td>
<td>92.6</td>
<td>1.420</td>
<td>0.105</td>
<td>0.137</td>
<td>0.096</td>
<td>0.173</td>
<td>1.831</td>
<td>1.025</td>
</tr>
<tr>
<td>1.5</td>
<td>91.9</td>
<td>1.390</td>
<td>0.099</td>
<td>0.125</td>
<td>0.090</td>
<td>0.181</td>
<td>1.807</td>
<td>1.028</td>
</tr>
<tr>
<td>2.0</td>
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**Note.** $Y_{CH_4}^0$ is the saturation mole fraction for pure CH$_4$, while $Y_{CH_4}$ is the saturation mole fraction above the equilibrium solution. Condensation in rising gas parcels ceases above $z = 28 \text{ km}$. 

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FIG. 3. CH$_4$ saturation mole fraction and condensate composition versus altitude for the nominal $p$–$T$ profile. Gas-phase saturation mole fractions above pure CH$_4$, $Y(CH_4,\text{pure})$, and above the equilibrium CH$_4$ + N$_2$ condensate, $Y(CH_4,\text{model})$, are plotted on the left. On the right the mole fraction of N$_2$ in the condensate predicted by our model, $X(N_2,\text{liquid})$, and its extension to altitudes where the liquid is metastable against freezing, $X(N_2,\text{meta-liq})$, are shown. The equilibrium composition of the solid solution, $X(N_2,\text{solid})$, from Thompson (1985) is also shown.
FIG. 4. Comparisons of pure-component properties, simple models, and the results of Thompson et al. (1990), Kouvaris and Flasar (1991) (hereafter referred to as TH90 and KF91, respectively), and the present model (a) Comparisons of CH$_4$ saturation mole fractions $Y_{CH_4}$. Profiles for pure CH$_4$, an ideal solution (Raoult's Law), the TH90 parameterization, the KF91 numerical integration, and the present model are shown. TH90 and the present results agree very closely. (b) Comparisons of N$_2$ mole fractions in the condensate $X_{N_2}$. Profiles for an ideal solution (Raoult's Law), Henry's law (see Kidnay et al. 1985), TH90, KF91, and the present model are shown. Deviations of TH90 and KF91 are more noticeable for liquid-phase compositions.

is more subject to biases caused by possible inaccuracies in the experimentally difficult measurement of equilibrium gas phase composition. While all three models do a reasonable job of predicting gas-phase saturation conditions, our present model is more strongly constrained and less prone to biases caused by high experimental $Y_{CH_4}$'s or other errors inherent in particular data sets. The actual $Y_{CH_4}$ is about 20% lower than that which would be in equilibrium with pure CH$_4$, and 25% higher than that which would be computed from Raoult's law.

In Fig. 4b we show the vertical profile of $X_{N_2}$ in the condensate. An ideal solution would have about 100% more N$_2$, while Henry's law would predict about 30% less than that computed from the models. The empirical parameterization of Thompson et al. (1990) is close to the line computed from our detailed model, matching it at the surface but progressively underestimating $X_{N_2}$ toward higher altitudes. The results of Kouvaris and Flasar (1991) are generally close, but deviate by ±5−10% at higher altitudes. This is probably due to the inaccuracies in $X_{N_2}$ in the data of Omar et al. (1962) seen in Fig. 2. (Kouvaris and Flasar note that their integration can still estimate $Y_i$ well, even with modest errors in $X_i$.) We believe the temperature dependence and consistency built into our model allows it to predict both $X_i$ and $Y_i$ well at low temperatures, without the inaccuracies in one or the other caused, in the other models, by strong dependence on problematic or sparse data.

Enthalpy of Condensation (Latent Heat)

For an ideal solution the enthalpy of condensation $\Delta H^c_i = \Sigma_i X_i \Delta H^c_i$, where $\Delta H^c_i$ is the value for pure i (Brown and Ziegler 1980, Table III). The actual value $\Delta H^c = \Delta H^c_i + H^E$, where $H^E$ is given by Eq. 8. In Fig. 5 we show the altitude profile of $\Delta H^c$ in Titan's atmosphere. Because $|\Delta H^c_i| > |\Delta H^c_{N_2}|$, the latent heat of condensation of an ideal CH$_4$ + N$_2$ solution is lower in magnitude (here, by about 10%) than that of pure CH$_4$. Since $H^E > 0$ (the computed excess enthalpy is endothermic), the actual value of $\Delta H^c$ is lower still. $X_{N_2}$ increases with altitude sufficiently rapidly to reverse the sense of altitude dependence of $\Delta H^c$ compared to the trend for pure CH$_4$.

IMPLICATIONS

Our thermodynamically constrained model is well suited to providing a best current estimate of saturation conditions, condensate compositions, and latent heats in Titan's atmosphere; these can be readily computed, or read from Table IV for the nominal atmospheric $p$−$T$ profile. We have also shown the levels of accuracy of the simpler parameterization of Thompson et al. (1990) and the partially parameterized numerical method of Kouvaris and Flasar (1991). (Because the model of Thompson et al. (1990) implicitly includes gas-phase nonideality and standard-state corrections within the parameters, its use may still be expeditious in some calculations.)
We list several types of studies which, as they reach a given level of sophistication, need to allow for the detailed behavior of the CH₄ + N₂ system.

- The saturation profile is changed, influencing the implications of models of CH₄ band structure in the near-infrared, where interband minima sample deep into the troposphere (Griffith et al. 1992). Limits on the abundance of CH₄ in the lower atmosphere placed by the T profile in the lowermost few km (Eshleman et al. 1983) are affected because of a different wet adiabatic lapse rate. Cloud microphysical and radiative-convective models (Toon et al. 1988, McKay et al. 1989) are affected by the reduction of latent heat and of the quantity of CH₄ gas thermal opacity in the troposphere.

- The refractive index and absorption properties of the cloud particles are changed. For a given amount of cloud thermal opacity in the CH₄ far-infrared collision-induced rotational transition (Thompson and Sagan 1984, Toon et al. 1988), the corresponding cloud mass will increase (Thompson 1985). The contribution to N₂ thermal opacity by dissolved N₂ in the cloud is small, but scattering models will be mildly influenced by the higher real, and by the lower (CH₄-dominated) imaginary, index of refraction of the cloud droplets.

- Conditions for nucleation and growth of cloud droplets are changed; a new complexity to cloud microphysics and precipitation is added by the fact that condensate falling through the atmosphere finds itself in disequilibrium with its surroundings, even if the atmosphere is locally saturated.

- New ramifications of certain measurements planned for the Cassini Huygens probe arise. The compositions of liquid tropospheric cloud droplets can be calculated from their refractive index, and compared with measured gaseous compositions to determine whether droplets are in local thermodynamic equilibrium. Departures will provide at least some constraints on growth versus sedimentation rates. Also, through the various effects listed above, modeling of the results of other Cassini probe and orbiter investigations will be intertwined with the vapor–liquid equilibrium in the atmosphere.

Titan presents a unique environment for study, with complex cloud thermodynamics, substantial expanses of liquid hydrocarbons probable at the surface (Lunine et al. 1983, Thompson 1985, Dubouloz et al. 1989), and many organic species, including hydrocarbons and nitriles, present as atmospheric gases (cf. Thompson et al. 1991), stratospheric condensates (cf. Sagan and Thompson 1984, Frère and Raulin 1990), minor ocean/lake solutes (Dubouloz et al. 1989), and surface sediments (Thompson et al. 1989; Thompson and Sagan 1992). New experimental efforts continue to be needed to provide accurate laboratory data of several types, so that physical models can confidently advance our understanding of this unique world.

### APPENDIX

#### Equation of State Calculations

We use a second-order virial equation of state (Eq. 5), with the virial coefficients of the mixture $B_{mi}$ and $C_{mi}$ defined (Eq. 6) in terms of pure-component and cross-coefficients $B_i$ and $C_{ik}$. Here we provide a means of calculating those coefficients.

We use the method of Hayden and O’Connell (1975) (HO75) to calculate all second virial coefficients and cross-coefficients. HO75 represent the interactions embodied in $B$ in the form

$$B_{tot} = B_{lw} + B_{nc} = b_0[f(T_s) + A \exp[\Delta H/(kT_s)]]$$

All of the above terms (in addition to Boltzmann’s constant $k$ and temperature $T$) are expressible as functions of four constants: dipole moment $\mu$, radius of gyration $R'$, critical temperature $T_c$, and critical pressure $p_c$. Computationally,

$$b_0 = \frac{2\pi}{3N_0\alpha^3}$$

where $N_0$ is Avogadro’s number, and the molecular interaction potential parameter

$$\sigma = (2.44 - \omega')(T_c/p_c)^{\frac{1}{3}}$$

where

$$\omega' = 0.006R' + 0.02087R'^2 - 0.00136R'^3$$

so $b_0 = f(R', T_c, p_c)$. The function

---

**FIG. 5.** Latent heats of condensation versus altitude for the nominal $p$-$T$ profile. Results for pure CH₄, an ideal solution having the composition of CH₄ + N₂ equilibrium condensate, and the present model are shown. The magnitude of $\Delta H_c$ is about 10% less than for pure CH₄.
where
\[ T_+ = \frac{1}{kT} - 1.6\omega \]
and the (other) molecular interaction potential parameter
\[ \epsilon = kT(0.748 + 0.91\omega) \]
so that \( f(T) = f(T; R, T_c, \rho_c) \).

For the second term,
\[ A = -0.3 - 0.05\mu^2 \text{ and } \Delta H = 1.99 + 0.2\mu^2, \]
where the reduced dipole moment
\[ \mu_* = \mu^2 / \sigma^3, \]
so (with the equations above) \( A \) and \( \Delta H = f(\mu, R, T_c, \rho_c) \).

The four constants needed to calculate pure-component second virial coefficients \( B \), are listed in Table V. The cross-coefficients \( B_{ij} \) are computed in the same way, except that the intermediate parameters in the computation \( \epsilon, \sigma, \omega, \) and \( \mu_* \) are computed from pure-component values according to the mixing rules:

- \( \epsilon_{ij} = 0.7(\epsilon_i + \epsilon_j) + 0.6(\epsilon_i^{-1} + \epsilon_j^{-1})^{-1} \)
- \( \sigma_{ij} = (\sigma_i \sigma_j)^{1/2} \)
- \( \omega_{ij} = 0.5(\omega_i + \omega_j) \)
- \( \mu_{ij} = \mu_i \sigma_i / \sigma_i^3 \)

[Our equation for \( \epsilon_i \) corrects Eq. (32) in HO75. Also, note that although the virial expansion used by HO75 is \( Z = 1 + B(p/RT) \), the second (but not higher) virial coefficients are identical in the \( v^{-1} \) and \( p/RT \) virial expansions.]

We compute the third virial coefficients for pure components \( C_{ii} \) using the method of Orbey and Vera (1983). They express these in the form
\[ C = \left( \frac{RT_{ci}}{p_c} \right) (F_0(T_i) + \omega F_1(T_i)), \]
where \( T_i = T/T_c \) is the reduced temperature and the functions \( F_0 \) and \( F_1 \) are given by
\[ F_0(T_i) = 0.01407 + 0.02432/T_i^{2.8} - 0.00313/T_i^{10.5}, \]
\[ F_1(T_i) = -0.02676 + 0.01770/T_i^{2.8} + 0.040/T_i^{10.5} \]
\[ - 0.003/T_i^{6.6} - 0.00228/T_i^{4.6}. \]

so \( C_{ii} = f(T_i; \omega, T_c, \rho_c) \). The "acentric factor" \( \omega \) is also tabulated in Table V.

There is no simple analog of the method of Hayden and O'Connell for computing the third virial cross-coefficients. In other modeling, we have found that an extension of the Prausnitz combining rules (Prausnitz 1969) can be used to define pseudo-critical parameters:

- \( T_{c,i} = (T_{c,i} T_{c,j})^{1/2} \)
- \( \omega_{ij} = \frac{2\omega_i + \omega_j}{3} \)
- \( v_{c,ij} = \frac{2Z_{c,i} + Z_{c,j}}{3} \)
- \( p_{c,ij} = \frac{RT_{c,i} Z_{c,ij}}{V_{c,ij}} \)

which we employ in the Orbey and Vera (1983) method to compute \( C_{ij} \) and \( C_{ij} \). At the low temperatures relevant here, the equation of state is much more sensitive to the second (\( B \)) coefficients than to the third (\( C \)) coefficients.

Finally, note that the virial equation of state can also be written
\[ Z = \frac{p}{RT} = 1 + B'(p/RT) + C'(p/RT)^2. \]

As already stated, the second virial coefficients are the same: \( B' = B \). However, the third virial coefficients in a \( p/RT \) expansion are related to those in a \( 1/\theta \) expansion by \( C' = C - B^2 \).

\section*{Vapor Pressure Equation}

Here we use a vapor pressure equation derived from "extended asymptotic behavior" by Iglesias-Silva et al. (1987) (IS87). This method is essentially an interpolation technique between the critical point and the triple point, where the equation must satisfy theoretical constraints at these two extremes.

The fundamental form is
\[ q(t) = (q_0(t)^N + q_1(t)^N)^{1/N}, \]
where
\[ q(t) = 1 + \frac{p(t) - p_c}{p_c - p_p}, \]
\[ t = \frac{T - T_c}{T_p - T_c}, \]
the \( p \) subscript represents triple point conditions, and the \( \varepsilon \) subscript represents critical point conditions. \( q_0(t) \) is the asymptotic form of the
vapor pressure near the triple point, and \( q_n(t) \) is the form near the critical point. The parameterized asymptotic forms chosen by IS87 are

\[
q_d(t) = a_0 + a_1 a_3(t + 1) \exp \left( \frac{-a_2 + b_0 R}{a_3 t + 1} \right)
\]

\[
q_r(t) = 2 - a_4(1 - t) + a_6(1 - t)^2 + a_7(1 - t)^3 + a_8(1 - t)^4.
\]

The identities

\[
a_0 = 1 - p_q / (p_c - p_p)
\]

\[
a_1 = -\left(\frac{a_0 - 1}{2}\right) e^z - \frac{h_0 R}{a_3 t + 1}
\]

\[
a_2 = \frac{b_0}{RT_p}
\]

\[
a_3 = \frac{(T_c - T_p) / T_p}{1 + \frac{b_1}{RT_p}}
\]

formally reduce the number of parameters to eight: \( N, \Theta, b_0, b_1, a_4, a_5, a_6, \) and \( a_7 \). IS87 chose

\[
N = 87T_p / T_c \quad \text{and} \quad \Theta = 0.2
\]

and infer the relationships

\[
a_4 = -0.11599104 + 0.29506258a_3 \quad \text{and} \quad 0.00021222a_5
\]

\[
a_6 = -0.01546028 + 0.08978160a_4 - 0.05322199a_7
\]

\[
a_7 = 0.05725757 - 0.06817687a_4 + 0.00047188a_5
\]

reducing the number of parameters to three: \( a_4, b_0, \) and \( b_1 \), so that eventually \( q = f(t; a_4, b_0, b_1; p_c, p_p, T_c, T_p) \). The latter seven parameters and constants are listed in Table V.

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REFERENCES


THERMODYNAMICS OF $N_2 + CH_4$ ON TITAN


